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(54) A polyimide film, a method for its manufacture and a polyimide film containing metal laminated plate

Polyimidfolie, ein Verfahren zu ihrer Herstellung, und eine mit Metallfolie verbundene Polyimidfolie

Film de polyimide, son procédé de préparation et un film de polyimide laminé avec une feuille métallique

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EP-A- 0 879 839	**WO-A-93/17069**

- **PATENT ABSTRACTS OF JAPAN vol. 098, no. 001, 30 January 1998 & JP 09 235373 A (DU PONT TORAY CO LTD), 9 September 1997,**
- **PATENT ABSTRACTS OF JAPAN vol. 017, no. 309 (C-1070), 14 June 1993 & JP 05 025273 A (KANEGAFUCHI CHEM IND CO LTD), 2 February 1993,**

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a polyimide film which has high elasticity, low thermal expansion properties equal to those of metals and low water absorption properties, a method for its manufacture and a metal laminated plate of improved curl containing the polyimide film as the base material.

BACKGROUND OF THE INVENTION

[0002] Polyimides that are obtained by condensation polymerization of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether have superior heat resistance and electrical insulating capacity and are used primarily for flexible printed circuit boards. Most recently, their uses have been expanded to semiconductor packages. High processability and capacity for high precision are required, a high modulus of elasticity, low thermal expansion characteristics like that of metals and low water absorbing capacity are sought as the characteristics of polyimides and various studies have been conducted. For example, in Japanese Patent Application Public Disclosure No. 60-210629 [1985], Japanese Patent Application Public Disclosure No. 64-16832 [1989], Japanese Patent Application Public Disclosure No. 64-16833 [1989], Japanese Patent Application Public Disclosure No. 64-16834 [1989], Japanese Patent Application Public Disclosure No. 1-131241 [1989] and Japanese Patent Application Public Disclosure No. 1-131242 [1989], an example of a three component polyimide comprised of pyromellitic dianhydride, 4,4'-diaminodiphenyl ether and p-phenylenediamine is described in which p-phenylenediamine is used in combination as the diamine component for the purpose of increasing the modulus of elasticity. Expansion to a four component polyimide can also be effected by adding 3,3'-4,4'-biphenyltetracarboxylic acid dianhydride to the aforementioned three-component system for the purpose of increasing the modulus of elasticity. Examples of four component polyimides are described in Japanese Patent Application Public Disclosure No. 59-164328 [1984] and Japanese Patent Application Public Disclosure No. 61-111359 [1986]. In addition, an attempt to improve the physical properties of four component polyimides by controlling the procedure of addition of the monomers during polymerization is presented, for example, in Japanese Patent Application Public Disclosure No. 5-25273 [1993]. Further, an attempt to improve physical properties by drawing during film making is described, for example, in Japanese Patent Application Public Disclosure No. 1-20238 [1989].

[0003] A high modulus of elasticity, low thermal expansion capacity equivalent to that of metals and low water absorbing capacity are necessary as characteristics for use in semiconductor packages as described above. Although the three-component polyimides that are obtained in Japanese Patent Application Public Disclosure No. 60-210629 [1985], Japanese Patent Application Public Disclosure No. 64-16832 [1989], Japanese Patent Application Public Disclosure No. 64-16833 [1989], Japanese Patent Application Public Disclosure No. 64-16834 [1989], Japanese Patent Application Public Disclosure No. 1-131241 [1989] and Japanese Patent Application Public Disclosure No. 1-131242 [1989] have a higher modulus of elasticity than the polyimides that are obtained from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether, a modulus of elasticity sufficient for use as semiconductor packages cannot be obtained. Further, with the four-component polyimides that are obtained in Japanese Patent Application Public Disclosure No. 59-164328 [1984] and Japanese Patent Application Public Disclosure No. 61-111359 [1986], it is necessary to use a large quantity of p-phenylenediamine for the purpose of obtaining a sufficient modulus of elasticity. As a result, there is the problem that the coefficient of thermal expansion becomes excessively lower than that of the metal. With the four component polyimide described in Japanese Patent Application Public Disclosure No. 5-25273 [1993], the modulus of elasticity and thermal expansion capacity are sufficient for this use. However, there is the problem that there is a high coefficient of water absorption. Further, with the three-component polyimide that is obtained in Japanese Patent Application Public Disclosure No. 1-20238 [1989], there are the problems in that the modulus of elasticity is markedly increased and that flexibility is lost as a result of drawing, that the coefficient of thermal expansion is considerably decreased and that there are great differences in thermal behavior from the metal when the film is affixed.

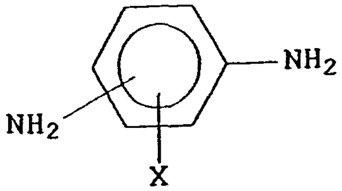
[0004] European Patent Application No. 97 108 876.0 (0 879 839) is prior art for the purposes of Article 54(3) and (4) EPC and discloses a polyimide copolymer containing a block polyimide component formed from a rigid aromatic diamine compound and an aromatic tetra-carboxylic acid compound and a random polyimide component formed from a flexible aromatic diamine compound and at least two different aromatic tetracarboxylic acid compounds. In this copolymer, the rigid aromatic diamine compound comprises 12 to 30 mole % of the total amount of aromatic diamine, and the flexible aromatic diamine compound comprises 70 to 88 mole % of the total amount of aromatic diamine.

[0005] Consequently, this invention has the objective of providing a polyimide film of high elasticity, low thermal expansion characteristics equal to those of metal and low water absorbing capacity, a method for its manufacture and metal laminated plates of improved curl in which it is the base material.

SUMMARY OF THE INVENTION

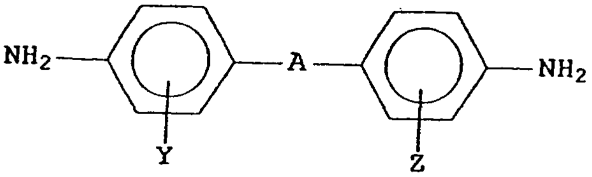
[0006] This invention provides a method of manufacture of a polyimide film having a birefringence less than 0.01 comprising a block component and a random component which are molecularly bonded, which solves the aforementioned problems, comprising the steps of:

(1) mixing 12 to 30 mol% based upon the total amount of aromatic diamine of a first rigid aromatic diamine compound of formula (I)



(I)

wherein X is a monovalent substituent group selected from hydrogen, halogen atoms, a carboxyl group, C_{1-6} alkyl groups and C_{1-6} alkoxy groups, and an aromatic tetracarboxylic acid compound in an organic solvent that is non-reactive with the reaction components for the time required for reaction, wherein the amount of the aromatic tetracarboxylic acid compound is 95 to 105 mol% relative to the amount of the aromatic diamine compound (I);
(2) adding 70 to 88 mol% based upon the total amount of aromatic diamine of a second flexible aromatic diamine compound of formula (II)



(II)

wherein Y and Z, which may be the same or different, are monovalent substituent groups selected from hydrogen, halogen atoms, a carboxyl group, C_{1-6} alkyl groups and C_{1-6} alkoxy groups; and A is a divalent group selected from -O-, -S-, -CO-, -SO-, $-SO_2-$ and $-CH_2-$, followed by addition of a first aromatic tetracarboxylic acid compound (A) and a second aromatic tetracarboxylic acid compound (B), which is different from (A), so that the total aromatic tetracarboxylic acid component and the total aromatic diamine component are in an essentially equimolar quantity, and mixing these substances for the time required for reaction, to form a copolymerized polyamidic acid solution;
(3) cyclizing the copolymerized polyamidic acid solution; and
(4) drawing the cyclized polyamidic acid solution in the lengthwise direction at a multiple of 1.05 to 1.5 and in the crosswise direction at a multiple of 1.05 to 2.0, eliminating the solvent and effecting formation to form the polyimide film.

[0007] The invention also relates to a metal laminated plate characterized in that the polyimide film of the invention is used as the base material and is laminated with metal.

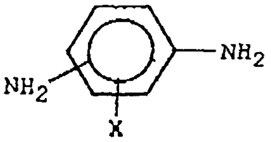
DETAILED DESCRIPTION OF THE INVENTION

[0008] The block component of the polyimide that forms the copolymerized polyimide manufactured according to this invention consists of repeated polyimide molecular chains that are obtained from one aromatic diamine compound having a rigid structure and one aromatic tetracarboxylic acid compound and is obtained by formation in the first stage of polymerization. The random component of the copolymerized polyimide is formed by reacting the aromatic diamine compound having a flexible structure and at least two or more aromatic tetracarboxylic acid compound in the second stage of polymerization. The polyimide film that has been formed by drawing a copolymerized polyimide that is formed by molecular bonding of the block component of the polyimide and the random component of the copolymerized polyimide that are obtained in this way can have the superior physical properties of high elasticity, low thermal expansion characteristics equivalent to those of metal and low water absorbing characteristics.
[0009] It is essential that the birefringence of the polyimide film that is obtained by drawing be controlled to less than

0.01 When the birefringence is greater than 0,01, the anisotropy of the film increases and curl readily occurs when it is affixed to the film. This is not desirable.

[0010] It is desirable that the coefficient of thermal expansion of the polyimide film that is obtained by drawing be controlled within a range of 10 to 22 ppm/°C. When it is outside of this range, differences in the thermal behavior of the metal, the IC chip and the epoxy base material occur and there are great changes in dimensions. There are instances in which this is undesirable.

[0011] Aromatic diamine compounds having a rigid structure that are used in this invention that can be cited include compounds as indicated by general formula (I) below.

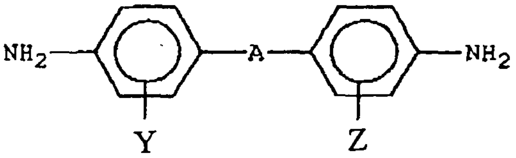


(I)

wherein X indicates a monovalent substitution group that can be selected from hydrogen, halogen groups, carboxyl groups, lower alkyl groups and lower alkoxy groups.

[0012] Among the aromatic diamine compounds having a rigid structure as indicated by general formula (I), it is desirable to use compounds in which X is hydrogen from the standpoint of increasing the modulus of elasticity of the polyimide film that is obtained. Of these compounds, the use of p-phenylenediamine is particularly desirable.

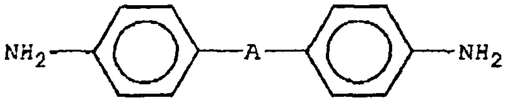
[0013] Aromatic diamine compounds having a flexible structure that are used in this invention that can be cited include compounds as indicated by general formula (II) below.



(II)

wherein Y and Z indicate monovalent substitution groups that are selected from hydrogen, halogen groups, carboxyl groups, lower alkyl groups and lower alkoxy groups and Y and Z may be substituted groups that arc the same or different; and A indicates a divalent coupled group that is selected from -O-, -S-, -CO-, -SO-, SO_2- and -CH_2-.)

[0014] Among the aromatic diamine compounds having a flexible structure as indicated by general formula (II), aromatic diamine compounds without any substitution groups except for amino groups as shown in formula (III) below are preferable from the standpoint of increasing the forming capacity of the polyimide film that is obtained.



(III)

(A indicates a divalent coupling group that is selected from -O-, -S-, -CO-, -SO-, -SO_2- and -CH_2-).

[0015] Of these, the use of 4,4'-diaminodiphenyl ether is particularly desirable.

[0016] The proportions of the aromatic diamine compounds that are used relative to the total aromatic diamine components are 12 mol % to 30 mol % of aromatic diamine compound having a rigid structure and 70 mol % to 88 mol % of aromatic diamine compound having a flexible structure. When the proportion of aromatic diamine having a rigid structure that is used is less than aforementioned proportion and when the proportion of aromatic diamine compound having a flexible structure is excessively great, the modulus of elasticity of the polyimide film that is obtained is decreased and its coefficient of thermal expansion is increased. This is not desirable. Further, when the proportion of aromatic diamine having a rigid structure used is greater than the aforementioned proportion and when the proportion of aromatic diamine compound having a flexible structure used is decreased, the coefficient of water absorption of the polyimide film is increased, its coefficient of thermal expansion is excessively decreased, its modulus of elasticity is excessively increased and formability is lost This is not desirable.

[0017] It is desirable that the aromatic tetracarboxylic acid compounds that are used may be one or more compounds selected from pyromellitic acid compounds, 3,3'-4,4'-biphenyltetracarboxylic acid compounds and 3,3'-4,4'-benzophenonetetracarboxylic acid compounds.

[0018] Aromatic tetracarboxylic acid compounds that can be used include pyromellitic acid or dianhydrides thereof as the pyromellitic acid compounds, 3,3'-4,4'-biphenyltetra-carboxylic acid or dianhydrides thereof as the 3,3'-4,4'-biphenyltetracarboxylic acid compounds and 3,3'-4,4'-benzophenonetetracarboxylic acid or dianhydrides thereof as the 3,3'-4,4'-benzophenone-tetracarboxylic acid compounds.

[0019] It is desirable that the proportions of the aromatic tetracarboxylic acid compounds that are used relative to the total aromatic diamine components may be 50 mol to 80 mol % of pyromellitic acid compounds and 20 mol % to 50 mol % of 3,3'-4,4'-biphenyltetracarboxylic acid compounds and/or 3,3'-4,4'-benzophenonetetracarboxylic acid compounds. When the proportion of 3,3'-4,4'-biphenyltetracarboxylic acid compounds and/or 3,3'-4,4'-benzophenonetetracarboxylic acid compounds used is less than the aforementioned proportion, the modulus of elasticity *of* the polyimide film that is obtained is decreased and the coefficient of water absorption is increased. This is not desirable. Further, when the proportion of 3,3'-4,4'-biphenyltetracarboxylic acid compounds and/or 3,3'-4,4'-benzophenonetetracarboxylic acid compounds used is greater than the aforementioned proportion, the gas permeability of the polyimide film that is obtained deteriorates, bubbles are formed on the surface of the film and the adhesive strength ofthe film is decreased. This is not desirable. The 3,3'-4,4'-biphenyltetra-carboxylic acid compounds and 3,3'-4,4'-benzophenonetetra-carboxylic acid compounds may be used independently or they may be used as mixtures.

[0020] Next, we shall describe the method of manufacture of the polyimide film of this invention. First, in order to form the block component of the polyimide, one aromatic diamine compound having a rigid structure and one aromatic tetracarboxylic acid are mixed for more than 1 hour in the first stage of polymerization in an organic solvent that is nonreactive with the reaction component. It is desirable that the ratio of aromatic tetracarboxylic acid relative to the aromatic diamine compound that is used should be 95 to 105 mol %. However, 97 to 100 mol % is preferable for forming the block component with good efficiency and for molecular bonding with the random component that is formed in the second stage.

[0021] Next, as the second stage of polymerization in order to form the random component of the copolymerized polyimide, an aromatic diamine compound having a flexible structure is added, after which the aromatic tetracarboxylic acid (A) is added and the materials are stirred for longer than 1 hour. Further, the different aromatic tetracarboxylic acid (B), i.e., (A) ≠ (B), is added in a quantity such that the total aromatic tetracarboxylic acid component and the total aromatic diamine component are essentially equal and the materials are stirred for longer than one hour. In such a series of polymerizations, a polyamidic acid solution in which the block polymerized polyamidic acid component and the random copolymerized polyamidic acid component that are formed in the first stage and the second stage, respectively, are molecularly bonded can be obtained. This polyamidic acid solution is then cyclized, after which drawing and elimination of the solvent, are effected, by which means the desired polyimide film can be obtained.

[0022] We shall now describe the drawing in said method of manufacture. First, the polyamidic acid that has been obtained in the series of reactions is subjected to chemical cyclization using a cyclization catalyst or a dehydrating agent or is subjected to thermal cyclization by a heat treatment, by which means a gel film of polyimide is obtained. Next, the end of the gel film is affixed and it is desirable that drawing is performed in the lengthwise direction at a multiple of 1,05 to 1.5 and in the crosswise direction at a multiple of 1.05 to 2.0. When biaxial drawing of this kind is performed, there is improvement of the mechanical properties and of the anisotropy of the polyimide film that is obtained. This is desirable.

[0023] The aromatic tetracarboxylic acids that may be used in the first stage of polymerization in said method of manufacture may be pyromellitic acid compounds, 3,3'-4,4'-biphenyltetracarboxylic acid compounds and 3,3'-4,4'-benzophenonetetracarboxylic acid compounds which may be used individually. When pyromellitic acid compounds are used, they increase the modulus of elasticity of polyimide films that are finally obtained. This is desirable. Aromatic diamine compounds having a rigid structure are used as *the* aromatic diamines.

[0024] In the second stage of polymerization, it is desirable to use one or more compounds selected from pyromellitic acid compounds, 3,3'-4,4'-biphenyltetracarboxylic acid compounds and 3,3'-4,4'-benzophenonetetracarboxylic acid compounds as the aromatic tetracarboxylic acid compounds. In order to increase the modulus of elasticity of the polyimide film that is finally obtained, it is desirable to use a combination of pyromellitic acid compounds and 3,3'-4,4'-biphenyltetracarboxylic acid compounds. An aromatic diamine compound having a flexible structure is used as the aromatic diamine component.

[0025] The solvents that are used in said method of manufacture include dimethyl sulfoxide, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N-methyl-2-pyrrolidone and dimethyl sulfone. They may be used individually or in mixtures.

[0026] The copolymerized polyamidic acid that is obtained by said method of manufacture is prepared in a proportion of 10 to 30 wt % in the aforementioned solvent.

[0027] When the copolymerized polyamidic acid that is obtained by said method of manufacture is cyclized and made into a copolymerized polyimide, this procedure may be performed by the chemical ring closure method in which dehydration is performed using a dehydrating agent and a catalyst or by the thermal ring closure method in which dehydration is performed thermally. Use of the chemical ring closure method is preferable because the modulus of elasticity of the polyimide film that is obtained is increased, because its coefficient of thermal expansion is decreased and because chemical etching capacity, which is required for TAB uses, can be conferred. The dehydrating agents that can be used include aliphatic acid anhydrides such as acetic anhydride and aromatic acid anhydrides such as phthalic anhydride. They may be used individually or in mixtures. The catalysts that may be used include heterocyclic tertiary amines such as pyridine, picoline and quinoline, aliphatic tertiary amines such as triethylamine and aromatic tertiary amines such as N,N-dimethylaniline. They may be used individually or in mixtures.

[0028] The metal laminated plate of this invention may be a three-layer structure in which electroconductive metal foil is laminated on the surface of the polyimide film, which is the base material, through the use of an adhesive agent such as a polyester base, an acrylic base, an epoxy base or a polyimide base or it may be a two-layer structure in which an electroconductive metal foil is laminated directly on the surface of the polyimide film without the use of an adhesive agent.

EXAMPLES

[0029] We shall now describe this invention in specific terms by means of examples.

GLOSSARY :	
PPD	p-phenylenediamine
ODA	4,4'-diaminophenyl ether
PMDA	pyromellitic dianhydride
BPDA	3,3'-,4,4'-diphenyltetracarboxylic dianhydride
BTDA	3,3'-4,4'-dibenzophenonetetracarboxylic dianhydride
DMAc	N,N-dimethylacetamide.

EXAMPLE 1

[0030] 239.1 g of DMAc were introduced into a 500 ml separable flask, 1.870 g (0.0173 mole) of PPD and 3.659 g (0.0168 mole) of PMDA were then introduced and a reaction was carried out for 1 hour at normal temperature and normal pressure. Next, 25.398 g (0.1268 mole) of ODA were introduced and the mixture was stirred until it was uniform, after which 8.481 g (0.0288) of BPDA were added and a reaction was carried out for 1 hour. Next, 21.491 g (0.0985 mole) of PMDA were added and a reaction was carried out for an additional 1 hour, with a polyamidic acid solution being obtained. The molar ratios of each raw material added in this polymerization were in the proportions shown in Table 1 and the total weight of solid component *was* prepared to 60.9 g. 15 g of this polyamidic acid solution were placed on a polyester film of 125 μm in thickness, after which the material was rotated for 1 minute at a rotational speed of 2500 rpm with a 1H-360A spin coater manufactured by Mikasa. Next, it was immersed for 10 minutes in a mixed solution of acetic anhydride and β-picoline, with an imidation reaction being effected, after which the polyimide gel film was peeled from the polyester film, the end of the gel film was pinned and drawing was performed 1.15 times in the lengthwise direction and 1.30 times in the crosswise direction. Following that, it was desiccated by heating for 20 minutes at 300°C and then for 5 minutes at 400°C. The pinning was removed, with a polyimide film of approximately 25 μm in thickness being obtained. The properties of this film were evaluated and the results are shown in Table 1.

[0031] The properties were evaluated by the following methods.

Evaluation methods:

[0032]

(1) Modulus of elasticity
Equipment: RTM-250
Drawing speed: 100 mm/min
Load: 10 kg
(2) Coefficient of thermal expansion
Equipment: TMA-50
Determination temperature range: 50 to 200°C

Temperature elevation speed: 10°C/min

(3) Coefficient of water absorption

The material was allowed to stand for 2 days in a desiccator in an atmosphere at 98% humidity and the evaluation was made in terms of the % of weight increase relative to the original weight.

(4) Birefringence

Equipment: KOBRA-21ADH

Light source: Sodium lamp

Angle of incidence: 0°

Determination formula: ΔN_{xy} = (retardation)/film thickness

(5) Evaluation of amount of curl of the metal laminated plate

[0033] An epoxy base adhesive agent was applied to the polyimide film and copper film was affixed to it at a temperature of 130°C. Following that, the temperature was raised to a maximum temperature of 160°C to harden the adhesive agent, the metal laminated plate that was obtained was cut to a sample size of 25 mm x 120 mm and it was allowed to stand for 24 hours at 60 RH %, after which the curl of the samples was measured. Curl was evaluated by placing the samples on level ground and by determining and averaging the heights of the squares. When the quantity of curl exceeded 3 mm, there were many instances in which handling in post-processing was extremely difficult when the product was to be used as metal laminated plate.

EXAMPLES 2 TO 10

[0034] Polyamidic acid solutions were obtained by the same procedure as in Example 1 with the aromatic diamine component and the aromatic tetracarboxylic acid component in the proportions shown in Table 1, after which drawing in the crosswise direction and lengthwise direction was performed at the multiples shown in Table 1 and the properties of the polyimide film obtained were evaluated by the same procedures as in Example 1. The results are shown in Table 1. The results for the amount of curl of the metal laminated plate for the polyimide film obtained in Example 3 (coefficient of thermal expansion: 17.5 ppm/°C; birefringence: 0.0094) are shown in Table 3.

EXAMPLE 11

[0035] A polyamidic acid solution was obtained by the same method as in Example 1 except that the BPDA was replaced by BTDA and the quantities of raw material added were in the proportions shown in Table 1. The physical properties of the polyamide film that were obtained were then evaluated by the same procedures as in Example 1. The results are shown in Table 1.

EXAMPLE 12

[0036] 239.1 g of DMAc were introduced into a 500 ml separable flask, PPD and BPDA were then introduced and a reaction was carried out for 1 hour at normal temperature and normal pressure. Next, ODA was introduced and the mixture was stirred until it was uniform, after which BPDA was added and a reaction was carried out for 1 hour. Next PMDA was added and the reaction was carried out for an additional hour, with a polyamidic acid solution being obtained. The quantities of each raw material that were added in this polymerization were in the proportions shown in Table 1. The total weight of the solid component was prepared to 60.9 g. Following that, the procedures for obtaining the polyimide film from the polyamidic acid solution were performed in the same way as in Example 1. Table 1 shows the results of the evaluations of the physical properties of the polyimide film.

COMPARATIVE EXAMPLE 1

[0037] The aromatic diamine component and the aromatic tetracarboxylic acid component were reacted and subjected to imidation in the same proportions and by the same procedures as in Example 1, after which the ends were pinned without drawing and desiccation was carried out by heating for 20 minutes at 300°C and then for 5 minutes at 400°C. The pinning was then removed and a polyimide film of approximately 25 μm in thickness was obtained. Table 2 shows the results of the evaluations of the physical properties of this film.

COMPARATIVE EXAMPLE 2

[0038] 239.1 g of DMAc were introduced into a 500 ml separable flask, ODA and PMDA were then added, a reaction was carried out for 1 hour in normal temperature and normal pressures and a polyamidic acid solution was obtained.

The molar ratio of ODA and PMDA was essentially 1:1. The total weight of the solid component was prepared to 60.9 g. Following that, the polyimide film that was obtained from the polyamidic acid solution was drawn in the crosswise direction and lengthwise direction at the multiples shown in Table 2. The physical properties of the polyimide film that was obtained were evaluated by the same procedures as in Example 1. The results of the evaluations are shown in Table 2.

COMPARATIVE EXAMPLE 3

[0039] 239.1 g of DMAc were introduced into a 500 ml separable flask, PPD and PMDA were added and a reaction was carried out for 1 hour at normal temperature and normal pressure. Next, ODA was introduced and the mixture was stirred until it was uniform, after which PMDA was added, a reaction was carried out for 1 hour and a polyamidic acid solution was obtained. The quantities of each raw material that were added in this polymerization were in the proportions shown in Table 2. The total weight of the solid component was 60.9 g. Following that, the polyamide film, which was obtained from the polyamidic acid solution, was drawn in the crosswise direction and the lengthwise direction in the multiples shown in Table 2. The other procedures were performed in the same way as in Example 1. The results of the evaluations of the physical properties of the polyimide film that were obtained are shown in Table 2. Table 3 shows the results that were obtained for the amount of curl of the metal laminated plate containing the polyimide film.

COMPARATIVE EXAMPLE 4

[0040] 239.1 g of DMAc were introduced into a 500 ml separable flask, PPD, ODA, BPDA and PMDA were then added in sequence, a reaction was performed for 2 hours at normal temperature and normal pressure and a polyamidic acid solution was obtained. The quantities of each raw material that were added in this polymerization were in the proportions shown in Table 2. The total weight of the solid component was adjusted to 60.9 g. Following that, the polyimide film that was obtained from the polyamidic acid solutions was drawn in the crosswise direction and the lengthwise direction in the multiples shown in Table 2. The other procedures were performed in the same way as in Example 1. Table 2 shows the results of the evaluations of the physical properties of the polyimide film that were obtained.

Table 1

Example	1	2	3	4	5	6
Type added and proportion (molar ratio*)	PPD 12.0 PMDA 11.6 ODA 88.0 BPDA 20.0 PMDA 68.4	PPD 12.0 PMDA 11.6 ODA 88.0 BPDA 30.0 PMDA 58.4	PPD 12 PMDA 12 ODA 88 BPDA 50 PMDA 38	PPD 18.0 PMDA 17.8 ODA 82.0 BPDA 30.0 PMDA 52.2	PPD 20.0 PMDA 19.4 ODA 80.0 BPDA 40.0 PMDA 40.6	PPD 25 PMDA 25 ODA 75 BPDA 20 PMDA 55
Drawing multiple in lengthwise direction	1.15	1.15	1.15	1.15	1.30	1.15
Drawing multiple in crosswise direction	1.30	1.30	1.30	1.30	1.50	1.30
Modulus of elasticity (kg/mm^2)	535	540	570	585	615	635
Coefficient of thermal expansion (ppm/°C)	18.6	18.8	17.5	16.3	14.8	11.7
Water absorption (%)	1.8	1.7	1.5	1.7	1.6	2.0
Birefringence	0.0090	0.0090	0.0094	0.0084	0.0073	0.0077

Example	7	8	9	10	11	12
Type added and proportion (molar ratio*)	PPD 25.0 PMDA 24.8 ODA 75.0 BPDA 25.0 PMDA 50.2	PPD 25.0 PMDA 24.8 ODA 75.0 BPDA 35.0 PMDA 40.2	PPD 30.0 PMDA 29.1 ODA 70.0 BPDA 25.0 PMDA 45.9	PPD 30.0 PMDA 29.1 ODA 70.0 BPDA 35.0 PMDA 35.9	PPD 25.0 PMDA 24.3 ODA 75.0 BPDA 25.0 PMDA 50.7	PPD 25.0 PMDA 24.8 ODA 75.0 BPDA 9.2 PMDA 66.0
Drawing multiple in lengthwise direction	1.15	1.15	1.15	1.15	1.15	1.15
Drawing multiple in crosswise direction	1.30	1.30	1.30	1.30	1.30	1.30
Modulus of elasticity (kg/mm^2)	650	660	680	660	605	620
Coefficient of thermal expansion (ppm/°C)	12.0	12.5	10.2	10.8	12.5	20.5
Water absorption (%)	1.9	1.7	2.1	2.0	2.1	1.5
Birefringence	0.0078	0.0083	0.0080	0.0078	0.0085	0.0082

*Molar ratios in the table indicate, respectively:

mol % in total aromatic diamine component;

mol % in total aromatic tetracarboxylic acid component.

Table 2

Comparative Example	1		2		3		4	
Type added and proportion (molar ratio*)	PPD PMDA ODA BPDA PMDA	12.0 11.6 88.0 20.0 68.4	ODA PMDA	100	PPD PMDA ODA PMDA	12.0 11.6 88.0 88.4	PPD ODA BPDA PMDA	25 75 25 75
Drawing multiple in lengthwise direction	1.00		1.20		1.30		1.15	
Drawing multiple in crosswise direction	1.00		1.30		1.30		1.30	
Modulus of elasticity (kg/mm^2)	488		360		490		450	
Coefficient of thermal expansion (ppm/°C)	21.0		26.0		16.0		23.5	
Water absorption (%)	2.2		2.4		2.4		2.0	
Birefringence	0.0020		0.022		0.019		0.0090	

*Molar ratios in the table indicate, respectively:
mol % in total aromatic diamine component;
mol % in total aromatic tetracarboxylic acid component.

Table 3 -

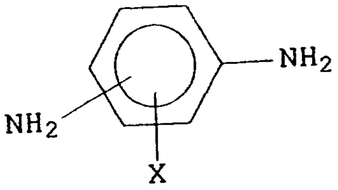
Evaluation of Metal Laminated Plate		
	Example	Comparative Example
Coefficient of thermal expansion (ppm/°C)	17.5	16.0
Birefringence	0.0094	0.019
Amount of curl (mm)	0.5	3.5

[0041] The polyimide film that is obtained in this invention is a copolymerized polyimide that is constituted of a block polymerized polyimide component and a random polymerized polyimide component, which are molecularly bonded, and when it is drawn its birefringence is less than 0.1 and its coefficient of thermal expansion is preferably 10 to 22 ppm/°C, showing improved mechanical properties. It can have both low thermal expansion properties and low water absorbing properties, and furthermore the amount of curl of the metal laminated plate can be decreased. Therefore, it can function satisfactorily when it is used for semiconductor packages requiring high dimension stability and high processability.

Claims

1. A method for the manufacture of polyimide film of a birefringence less than 0.01 comprising a block component and a random component which are molecularly bonded, comprising the steps of:

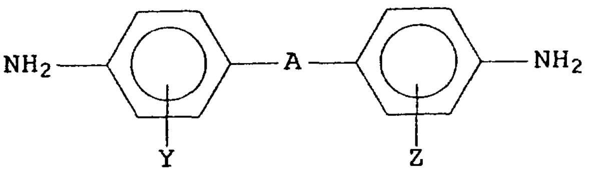
(1) mixing 12 to 30 mol% based upon the total amount of aromatic diamine of a first rigid aromatic diamine compound of formula (I)



(I)

wherein X is a monovalent substituent group selected from hydrogen, halogen atoms, a carboxyl group, C_{1-6} alkyl groups and C_{1-6} alkoxy groups, and an aromatic tetracarboxylic acid compound in an organic solvent that is nonreactive with the reaction components for the time required for reaction, wherein the amount of the aromatic tetracarboxylic acid compound is 95 to 105 mol% relative to the amount of the aromatic diamine compound (I) ;

(2) adding 70 to 88 mol% based upon the total amount of aromatic diamine of a second flexible aromatic diamine compound of formula (II)



(II)

wherein Y and Z, which may be the same or different, are monovalent substituent groups selected from hydrogen, halogen atoms, a carboxyl group, C_{1-6} alkyl groups and C_{1-6} alkoxy groups; and A is a divalent group selected from addition of a first aromatic tetracarboxylic acid compound (A) and a second aromatic tetracarboxylic acid compound (B), which is different from (A), so that the total aromatic tetracarboxylic acid component and the total aromatic diamine component are in an essentially equimolar quantity, and mixing these substances for the time required for reaction, to form a copolymerized polyamidic acid solution;

(3) cyclizing the copolymerized polyamidic acid solution; and

(4) drawing the cyclized polyamidic acid solution in the lengthwise direction at a multiple of 1.05 to 1.5 and in the crosswise direction at a multiple of 1.05 to 2.0, eliminating the solvent and effecting formation to form the polyimide film.

2. The method of claim 1 wherein cyclization is effected by a chemical cyclization method using a cyclization catalyst and a dehydrating agent.

3. The method of claim 1 wherein X is hydrogen in the compound of formula (I).

4. The method of claim 1 wherein the compound of formula (I) is *p*-phenylenediamine.

5. The method of claim 1 wherein Y and Z are both hydrogen in the compound of formula (II).

6. The method of claim 1 wherein the compound of formula (II) is 4,4'-diaminodiphenyl ether.

7. The method of any preceding claim wherein the aromatic tetracarboxylic acid compounds are selected from pyromellitic acid compounds, 3,3'-4,4'-biphenyltetracarboxylic acid compounds and 3,3'-4,4'-benzophenonetetracarboxylic acid compounds.

8. The method of claim 7 wherein the pyromellitic acid compounds constitute from 50 mol% to 80 mol% of the total aromatic tetracarboxylic acid component and wherein the 3,3'-4,4'-biphenyltetracarboxylic acid compounds and/or the 3,3'-4,4'-benzophenonetetracarboxylic acid compounds constitute from 20 mol% to 50 mol% of the total aromatic tetracarboxylic acid component.

9. A metal laminated plate comprising a polyimide film having laminated thereto a metal layer, wherein the polyimide film is manufactured according to any one of claims 1 to 8.

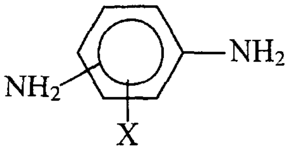
10. The metal laminated plate of claim 9 wherein the metal layer is an electroconductive metal foil.

11. The metal laminated plate of claim 9 or claim 10 wherein an adhesive agent is present between the polyimide layer and the metal layer.

Patentansprüche

1. Verfahren zur Herstellung von Polyimidfolie mit einer Doppelbrechung von weniger als 0,01, umfassend eine Blockkomponente und eine statistische Komponente, welche molekular verknüpft sind, umfassend die Schritte:

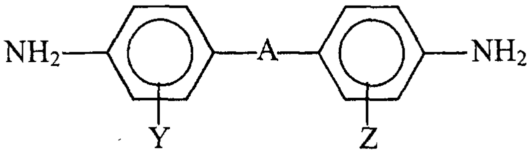
   (1) Mischen von 12 bis 30 Mol-%, bezogen auf die Gesamtmenge von aromatischem Diamin, einer ersten starren aromatischen Diaminverbindung der Formel (I)

   (I)

   in der X eine einwertige Substituentengruppe, ausgewählt aus Wasserstoff, Halogenatomen, einer Carboxylgruppe, C_{1-6}-Alkylgruppen und C_{1-6}-Alkoxygruppen, ist, und einer aromatischen Tetracarbonsäureverbindung in einem organischen Lösungsmittel, das nicht mit den Reaktionskomponenten reaktiv ist, für die zur Reaktion erforderliche Zeit, wobei die Menge der aromatischen Tetracarbonsäureverbindung 95 bis 105 Mol-% relativ zu der Menge der aromatischen Diaminverbindung (I) ist,

   (2) Hinzufügen von 70 bis 88 Mol-%, bezogen auf die Gesamtmenge von aromatischem Diamin, einer zweiten flexiblen aromatischen Diaminverbindung der Formel (II)

   (II)

   wobei Y und Z, welche gleich oder verschieden sein können, einwertige Substituentengruppen, ausgewählt aus Wasserstoff, Halogenatomen, einer Carboxylgruppe, C_{1-6}-Alkylgruppen und C_{1-6}-Alkoxygruppen, sind; und A eine zweiwertige Gruppe, ausgewählt aus -O-, -S-, -CO-, -SO-, $-SO_2-$ und $-CH_2-$, ist, gefolgt von der Zugabe einer ersten aromatischen Tetracarbonsäureverbindung (A) und einer zweiten aromatischen Tetracarbonsäureverbindung (B), welche von (A) verschieden ist, ist, so daß die gesamte aromatische Tetracarbonsäurekomponente und die gesamte aromatische Diaminkomponente in einer im wesentlichen äquimolaren Menge sind, und Mischen dieser Stoffe für die zur Reaktion erforderliche Zeit, um eine copolymerisierte Polyamidsäurelösung zu erzeugen;

   (3) Cyclisieren der copolymerisierten Polyamidsäurelösung; und

   (4) Ziehen der cyclisierten Polyamidsäurelösung in der Längsrichtung mit einem Mehrfachen von 1,05 bis 1,5 und in der Querrichtung mit einem Mehrfachen von 1,05 bis 2,0, Beseitigen des Lösungsmittels und Bewirken einer Formung, um die Polyimidfolie zu formen.

2. Verfahren nach Anspruch 1, wobei Cyclisierung durch ein chemisches Cyclisierungsverfahren unter Verwendung eines Cyclisierungskatalysators und eines Dehydratisierungsmittels bewirkt wird.

3. Verfahren nach Anspruch 1, wobei in der Verbindung der Formel (I) X Wasserstoff ist.

4. Verfahren nach Anspruch 1, wobei die Verbindung der Formel (I) p-Phenylendiamin ist.

5. Verfahren nach Anspruch 1, wobei in der Verbindung der Formel (II) Y und Z beide Wasserstoff sind.

6. Verfahren nach Anspruch 1, wobei die Verbindung der Formel (II) 4,4'-Diaminodiphenylether ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die aromatischen Tetracarbonsäureverbindungen

aus Pyromellitsäureverbindungen, 3,3'-4,4'-Biphenyltetracarbonsäureverbindungen und 3,3'-4,4'-Benzophenontetracarbonsäureverbindungen ausgewählt sind.

8. Verfahren nach Anspruch 7, wobei die Pyromellitsäureverbindungen 50 Mol-% bis 80 Mol-% der gesamten aromatischen Tetracarbonsäurekomponente bilden und wobei die 3,3'-4,4'-Biphenyltetracarbonsäureverbindungen und/oder die 3,3'-4,4'-Benzophenontetracarbonsäureverbindungen 20 Mol-% bis 50 Mol-% der gesamten aromatischen Tetracarbonsäurekomponente bilden.

9. Mit Metall laminierte Folie, umfassend eine Polyimidfolie mit einer darauf laminierten Metallschicht, wobei die Polyimidfolie nach einem der Ansprüche 1 bis 8 hergestellt wird.

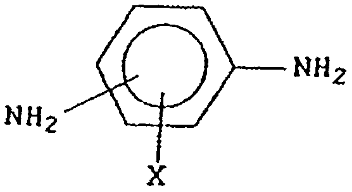
10. Mit Metall laminierte Folie nach Anspruch 9, wobei die Metallschicht eine elektrisch leitende Metallfolie ist.

11. Mit Metall laminierte Folie nach Anspruch 9 oder Anspruch 10, wobei ein Klebemittel zwischen der Polyimidschicht und der Metallschicht vorhanden ist.

Revendications

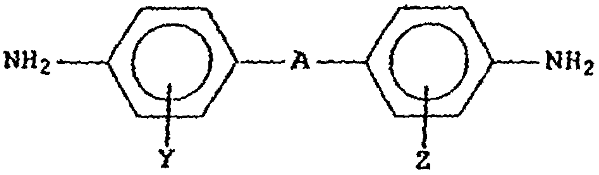
1. Procédé de fabrication d'un film de polyimide d'une biréfringence inférieure à 0,01 comprenant un composant en masse et un composant aléatoire qui sont moléculairement liés, comprenant les étapes de :

(1) mélange de 12 à 30% en mole sur base de la quantité totale de diamine aromatique d'un premier composé de diamine aromatique rigide de formule (I)



(I)

dans laquelle X est un groupement substituant monovalent choisi parmi les atomes d'hydrogène, d'halogène, un groupement carboxyle, des groupements alkyle en C_1-C_6 et des groupements alkoxy en C_1-C_6, et un composé d'acide tétracarboxylique aromatique dans un solvant organique qui est non réactif avec les composants de la réaction pendant le temps requis pour la réaction, dans laquelle la quantité de composé d'acide tétracarboxylique est 95 à 105% en mole, par rapport à la quantité du composé de diamine aromatique (I) ;
(2) addition de 70 à 88% en mole sur base de la quantité totale de diamine aromatique d'un second composé de diamine aromatique flexible de formule (II)



(II)

dans laquelle Y et Z, qui peuvent être identiques ou différents, sont des groupements substituants monovalents choisis parmi les atomes d'hydrogène, d'halogène, un groupement carboxyle, des groupements alkyle en C_1-C_6 et des groupements alkoxy en C_1-C_6; et A est un groupement divalent choisi parmi l'addition d'un premier composé d'acide tétracarboxylique aromatique (A) et un second composé d'acide tétracarboxylique aromatique (B), qui est différent de (A), si bien que le composant d'acide tétracarboxylique aromatique total et le composant de diamine aromatique total sont dans une quantité pratiquement équimolaire, et le mélange de ces substances pendant le temps requis pour la réaction, pour former une solution d'acide de polyamide

copolymérisé ;
(3) cyclisation de la solution d'acide de polyamide copolymérisé ; et
(4) étirage de la solution d'acide de polyamide cyclisé dans la direction de la longueur à un multiple de 1,05 à 1,5 et dans la direction croisée à un multiple de 1,05 à 2,0, en éliminant le solvant et en effectuant la formation du film de polyimide.

2. Procédé selon la revendication 1 dans lequel la cyclisation est effectuée par un procédé de cyclisation chimique en utilisant un catalyseur de cyclisation et un agent déshydratant.

3. Procédé selon la revendication 1 dans lequel X est hydrogène dans le composé de formule (I).

4. Procédé selon la revendication 1 dans lequel le composé de formule (I) est la p-phénylènediamine.

5. Procédé selon la revendication 1 dans lequel Y et Z sont tous les deux hydrogène dans le composé de formule (II).

6. Procédé selon la revendication 1 dans lequel le composé de formule (II) est le 4,4'-diaminodiphényléther.

7. Procédé selon l'une quelconque des revendications précédentes dans lequel les composés d'acide tétracarboxylique aromatique sont choisis parmi les composés d'acide pyromellitique, les composés d'acide 3,3',4,4'-biphényltétracarboxylique et les composés d'acide 3,3',4,4'-benzophénonetétracarboxylique.

8. Procédé selon la revendication 7 dans lequel les composés d'acide pyromellitique constituent de 50% en mole à 80% en mole du composant d'acide tétracarboxylique aromatique total et dans lequel les composés d'acide 3,3',4,4'-biphényltétracarboxylique et/ou les composés d'acide 3,3',4,4'-benzophénonetétracarboxylique constituent de 20% en mole à 50% en mole du composant d'acide tétracarboxylique aromatique total.

9. Plaque de métal laminé comprenant un film de polyimide ayant été laminé sur une couche de métal, dans laquelle le film de polyimide est fabriqué selon l'une quelconque des revendications 1 à 8.

10. Plaque de métal laminé selon la revendication 9 dans laquelle la couche de métal est une feuille de métal électroconductrice.

11. Plaque de métal laminé selon la revendication 9 ou la revendication 10 dans laquelle un agent adhésif est présent entre la couche de polyimide et la couche de métal.